THE RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM (RCCE) METHOD: A REDUCTION TECHNIQUE FOR COMPLEX KINETIC MODELS

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ABSTRACT

The method of Rate-Controlled Constrained-Equilibrium (RCCE) offers great potentials for modelling kinetic systems involving unknown kinetic pathways and parameters. It is a logical extension of classical thermodynamics and involves local maximization of entropy or minimization of a relevant free energy at any time during the non-equilibrium evolution of the system subject to a set of transient kinetic constraints. Constraints are imposed by slow rate-limiting kinetics. Consistent with classical thermodynamics, it is conjectured that the number of required constraints to describe the observed macroscopic kinetic behaviour is far smaller than the number of species in the system. . We present a review of application of the method to chemical kinetic modelling of combustion of H_2, C_1 and C_2 hydrocarbon fuels. The rate equations have been cast in terms of constraint potentials, once the values of which are known, the concentration of all species can be calculated immediately. Three kinetic systems have been studied: H_2/O_2, CH_4/air and C_2H_5OH/air mixtures. The detailed kinetic models include 9, 60 and 68 species along with 19, 352 and 383 chemical reactions, while their corresponding RCCE models involve 6, 16 and 16 constraints, respectively.

INTRODUCTION

The development of kinetic models for describing the time evolution of chemically reacting systems is a fundamental objective of chemical kinetics. Such models can easily include several hundred of species and several thousands of reactions for heavy hydrocarbon fuels. The fact that the equations governing the dynamics under such models are highly stiff necessitates the development of tools to reduce the complexity of the model while maintaining the degree of detail of predictions. Many approaches for this problem have been proposed over the last two decades among which are the Quasi-Steady State Approximation QSSA [1], Partial Equilibrium Approximation PEA [2], Intrinsic Low Dimensional Manifolds (ILDM) [3], Computational Singular Perturbation (CSP) [4], Adaptive Chemistry [5], Directed Relation Graph (DRG) [6], ICE-PIC method [7], and Rate-Controlled Constrained-Equilibrium (RCCE) [8].

Perhaps the most appealing feature of RCCE, as has also been explained in [9] is that, contrary to all dimension reduction models in which the constrained equilibrium assumption is not used, it is not necessary to start with a detailed kinetic model (DKM) which must then be simplified by various mathematical approximations. Instead, one starts with a small number of constraints, to which more constraints can be added, if necessary, to improve the accuracy of the calculations. The number of constraints needed to describe the dynamic state of the system within experimental accuracy can be very much smaller than the number of species in the system.
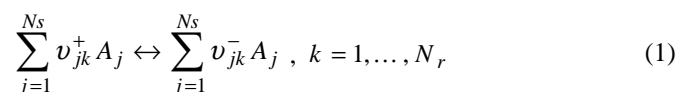
Therefore fewer reactions are needed to describe the system's evolution. Given the fact that in the entire body of thousands of chemical reactions perhaps less than hundred have rate constants known better than a factor of two, this feature of RCCE could help remove a great deal of uncertainty from the system by properly invoking the constrained-equilibrium assumption. Reactions which do not change any constraint are in constrained-equilibrium and need not to be specified. Nonetheless, the successful implementation of the RCCE method depends critically on the choice of constraints and knowledge of the rates of the constraints-changing reactions is required.

In this paper we use the method of RCCE to study the kinetics of H_2/O_2, CH_4/Air and C_2H_5OH/Air under constant volume, constant energy constraints. The aim of this paper is to present a set of constraints, for each kinetic model, based on a careful study of the kinetics of the system, which yields good agreements with the corresponding DKM over a wide range of initial temperatures and pressures.

GOVERNING EQUATIONS

The changes in the species composition of a system are the result of chemical reactions of the form

$$\sum_{j=1}^{Ns} \upsilon_{jk}^+ A_j \leftrightarrow \sum_{j=1}^{Ns} \upsilon_{jk}^- A_j \ , \ k=1,\ldots,N_r \qquad (1)$$

where A_j is the symbol of species j, N_r is the number of reactions, N_s is the number of species, υ_{jk}^+ and υ_{jk}^- are the forward and reverse stoichiometric coefficients of species j for reaction k.

For a given mechanism, the rate equation for an individual species j is given by

$$\frac{dN_j}{dt} = V \sum_{k=1}^{Nr} \upsilon_{jk} (r_k^+ - r_k^-) \ , \ j=1,\ldots,N_s \qquad (2)$$

where Nr is the number of reactions, $\upsilon_{jk} = \upsilon_{jk}^+ - \upsilon_{jk}^-$ is the net stoichiometric coefficient of species j in reaction k and r_k^+

and r_k^- are the forward and the reverse rates of reaction k defined as:

$$r_k^+ = k_k^+ \prod_{j=1}^{Ns} [N_j]^{\nu_{jk}^+} \,, \quad r_k^- = k_k^- \prod_{j=1}^{Ns} [N_j]^{\nu_{jk}^-}$$

The principle of detailed balance is also used to relate the forward and reverse reaction rate constants, k_k^+ and k_k^- through the reaction equilibrium constant.

Constrained Equilibrium

Constraints are assumed to be a linear combination of species composition present in the system, namely

$$C_i = \sum_{j=1}^{Ns} a_{ij} N_j \,, \quad i = 1,\ldots,N_c \tag{3}$$

where a_{ij} is the value of the ith constraint for the jth species and N_C is the number of constraints. The constrained equilibrium composition found by minimizing the Gibbs free energy subject to a set of constraints using the method of Lagrange multipliers is

$$N_j = V Q_j(T) \exp(-\sum_{j=1}^{Nc} a_{ij} \gamma_i) \tag{4}$$

where

$$Q_j(T) = \frac{p_0}{R_u T} \exp(-\mu_j^0(T))$$

is the partition function of species j. Also $\mu_j^0 = (h_j^0 - T s_j^0)/R_u T$ and γ_i are, respectively, the non-dimensional standard Gibbs free energy of species j and the constraint potential (Lagrange multiplier) conjugate to constraint i. It is important to notice that once the value of constraint potentials are obtained, the mole number of all species can be obtained through equation (4). This equation also established the reduced dimensional space as

$$N_j = N_j(T, V, \gamma_i)$$

which in conjunction with equation (4) yields

$$\frac{1}{N_j} \frac{dN_j}{dt} = \frac{1}{V} \frac{dV}{dt} + \left(\frac{E_j}{R_u T} \right) \frac{1}{T} \frac{dT}{dt} - \sum_{n=1}^{Nc} a_{nj} \frac{d\gamma_n}{dt} \tag{5}$$

Rate Equations for the Constraints

The rate equations of constraints can be determined by differentiating equation (3):

$$\frac{dC_i}{dt} = \sum_{j=1}^{Nc} a_{ij} \frac{dN_j}{dt} \,, \quad i=1,\ldots,N_C \tag{6}$$

and then using equation (2) to obtain

$$\frac{dC_i}{dt} = V \sum_{k=1}^{Nr} b_{ik} r_k \,, \quad i = 1., N_C \tag{7}$$

where

$$b_{ik} = \sum_{j=1}^{Nc} a_{ij} \nu_{jk}$$

is the change of constraint i due to reaction k. Since elements are conserved $b_{ik} = 0$ for $i=1,\ldots, N_e$ where N_e is the number of elements in the system. Upon integration of N_c rate equations (6), the N_c algebraic equations (3) and (4) must be solved to obtain the constrained-equilibrium mixture composition.

Constraint Potential Rate Equations

To avoid solving the algebraic equations involved in integration of constraints, the RCCE equations can be directly cast into the constraint potential forms, γ. Following similar steps detailed in [11], the equations governing the constraint potentials can be obtained by combining equations (5), (6) and (7) as follows

$$\sum_{n=1}^{Nc} C_{in} \frac{d\gamma_n}{dt} - \frac{C_{iV}}{V} \frac{dV}{dt} - \frac{C_{iT}}{T} \frac{dT}{dt} + \sum b_{ik} (r_k^+ - r_k^-) = 0 \tag{8}$$

where

$$C_{in} = \sum_{j=1}^{Ns} a_{ij} a_{nj} [N_j] \,,$$

$$C_{iV} = \sum_{j=1}^{Ns} a_{ij} [N_j] \,,$$

$$C_{iT} = \sum_{j=1}^{Ns} a_{ij} \frac{E_j}{RT} [N_j] \,,$$

Integration of equations, either (2), (7) or (8) need to be coupled with the equation of state and an appropriate energy equation.

Equation of state

For an ideal gas mixture the equation of state can be written:

$$pV = \sum_{j=1}^{Nsp} N_j RT \tag{9}$$

Energy Equation

For an ideal gas mixture, the energy can be written:

$$E = \sum_{j=1}^{Ns} N_j e_j(T) \tag{10}$$

where $e_j(T)$ is the energy per unit mole of species j. Also, the energy equation for an adiabatic, closed homogeneous system is:

$$\frac{dE}{dt} = -p \frac{dV}{dt} \tag{11}$$

Obviously, energy remains constant during an adiabatic constant volume process, while for an adiabatic constant pressure process enthalpy, i.e. $H=E+pV$, is conserved. Substituting relation (10) into equation (11), one obtains

$$\frac{dE}{dt} = \sum_{j=1}^{Ns} E_j \frac{d\dot{N}_j}{dt} + (\sum_{j=1}^{Ns} N_j C_{vj}) \frac{dT}{dt} \tag{12}$$

Also, replacing equation (5) into equation (12), the energy equation will have the following form:

$$\sum_{n=1}^{Nc} C_{en} \frac{d\gamma_n}{dt} + \frac{C_{eV}}{V}\frac{dV}{dt} + \frac{C_{eT}}{T}\frac{dT}{dt} - \frac{1}{V}\frac{dE}{dt} = 0 \qquad (13)$$

where

$$C_{en} = -\sum_{j=1}^{Ns} E_j a_{nj}[Nj] \ , \ C_{eV} = \sum_{j=1}^{Ns} E_j[Nj] \ ,$$

$$C_{eT} = \sum_{j=1}^{Ns} (C_{vj}T + \frac{E_j^2}{RT})[Nj] \ , \ \dot{E} = -\frac{p}{V}\frac{dV}{dt}$$

C_{vj} is the frozen molar heat capacity of species j at constant volume and p is pressure.

Equations (8), (9) and (13) form a set of N_c+2 equations for N_c+2 unknows (T, V, γ).

SELECTION OF CONSTRAINTS

The major area of research in RCCE is selection of kinetic constraints. Constraints could be either linear combinations of species or single species.

The main aim of our studies in RCCE is directed toward identifying the pattern of conversion of heavy hydrocarbons to smaller intermediates and ultimately to combustion products. In this paper we will discuss three chemical kinetic models, H_2/O_2 [13], CH_4/air and C_2H_5OH/air. The mechanism used for CH4/air studies is the GRI-mech3.0 [14] plus an additional nine C1 alkylperoxides and organic acids, with rates obtained from [15]. These species enable the model to be used at high pressures and low temperatures. Also, the C_2H_5OH mechanism is taken from [16].

Since the set of constraints required to model the chemistry of each kinetic model is different, we will only present one set of constraints, that for CH_4/air model. For more information about the other two kinetic models, please review [12-13]. Over the range of temperature and time scales of interest to combustion applications, the rates of ionization reactions are negligible compared to those of chemical reactions and the fixed constraints are the neutral elements of hydrogen, carbon, oxygen, nitrogen, designated by EH, EC, EO, EN.

Moreover, the slowest reactions controlling the chemical composition are three-body dissociation/recombination reactions and reactions which make and break valence bonds. Such reactions are slow in the endothermic direction because of the high activation energies required, and in the exothermic direction because of small three-body collision rates and small radical concentrations. They impose slowly varying time-dependent constraints on the number of moles, M, and the free valence, FV, of the system, respectively. A finite value of FV is a necessary condition for chain branching chemical reactions to proceed.

A third important time-dependent constraint is free oxygen, FO which is defined as any oxygen atom not directly bound to another oxygen atom. Free oxygen is imposed by slow OO bond-breaking reactions. An increase in FO is a necessary condition for the formation of the major reaction products of hydrocarbon oxidation, H_2O, CO_2 and CO.

Two additional time-dependent constraints which slightly improve the agreement between RCCE and DKM calculations under some conditions are: Moles of water radicals OHO $\equiv$ OH+O and moles of HCO+CO $\equiv$ DCO. The OHO constraint is a consequence of the relatively slow constraint-changing reaction RH+OH = R+H2O coupled with the fast reaction RH + O = OH+R which equilibrate OH and O. The DCO constraint is a consequence of the slow reaction CO + HO2 = CO2+OH coupled with the fast reaction HCO+O2 = CO+HO2 which equilibrate HCO and CO.

For systems involving the elements C, H, O and N, the nine constraints EC, EH, EO, EN, M, FV, FO, OHO, and DCO are independent of the initial reactants and may, therefore, be considered "universal" constraints.

In the present investigation of C_1 hydrocarbon oxidation, additional fuel-dependent constraints have been used. The first is a constraint on the fuel, FU, imposed by slow hydrogen – abstraction reactions of the type FU+O2=FR+HO2 and even slower dissociation/recombination of the type AB+M = A+B+M. This constraint is necessary to hold the system in its initial state. The second is a constraint on fuel radicals, FR, which is necessary to prevent the equilibration of forbidden exothermic global reactions such as CH3+2O2+2H2O => CO2+2H2O2+H2+H, which will otherwise convert fuel radical directly to products.

The third is a constraint on alkyl peroxides, APO$\equiv$ CH3OOH+CH3OO+CH2OOH, imposed by slow reactions which convert APO to hydro peroxides coupled with fast reactions which equilibrate the species comprising APO. The fourth is a constraint on alcohol plus formaldehyde, ALCD $\equiv$ CH3OH+CH3O+CH2OH+CH2O imposed by relatively slow reactions which generate/remove ALCD coupled with fast reactions which equilibrate the species comprising ALCD.

In the case of close to stoichiometric or rich conditions the path from C_1 to C_2 becomes important, which introduces an important structural constraint on the number of C-C bonds. A change in the value of this constraint is a necessary condition for formation or consumption of heavier hydrocarbons. This constraint controls the paths from C_2 to C_1 and vice versa. It takes the value of zero for C_1 species and the values of one and two for non-ether C_2 and C_3 molecules, respectively.

The next constraint identified is C_2H_6, which in a species map is directly connected to C_2H_5. The calculations of the rate of formation and consumption of C_2H_6 compared to the rate of consumption of C_2H_5 show that C_2H_6 is an important rate-controlling constraint over a wide range of thermodynamic conditions. Such calculations further show that the path from C_2H_5 to C_2H_4 can be assumed equilibrated subject to formation of C_2H_5 and consumption of C_2H_4. In other words, the slow reactions: C_2H_6+M = CH3+CH3+M, C_2H_6+O2=C_2H_5+HO2 and C_2H_4+O2=C_2H_3+HO2 coupled with fast reaction C_2H_5+O2=C_2H_4+HO2 impose C_2H_6 and C_2H_5 + C_2H_4 as extra C_2-specific constraints.

The set of constraints mentioned above, enables agreements too within 5% accuracy with DKM calculations over a a wide range of initial temperatures, pressures and equivalence ratios

RESULTS

H_2/O_2 Model

Ignitions of H_2/O_2, CH_4/air and C_2H_5OH/air have been studied using RCCE over a wide range of initial temperatures and pressures. Comparisons have also been made with DKM results. In all Figures, solid lines represent the DKM predictions while the dashed lines represent the RCCE predictions.

The H₂/O₂ chemical kinetic model includes 9 species and 19 chemical reactions. Ignition has been studied for initial temperatures varying from 900 K to 1500 K and initial pressures varying from 30 atm to 100 atm under stoichiometric conditions. the RCCE calculations were carried out under 6 constraints, namely EH, EO, EN, M, FV and FO. Results are shown in figures 1 and 2 respectively.
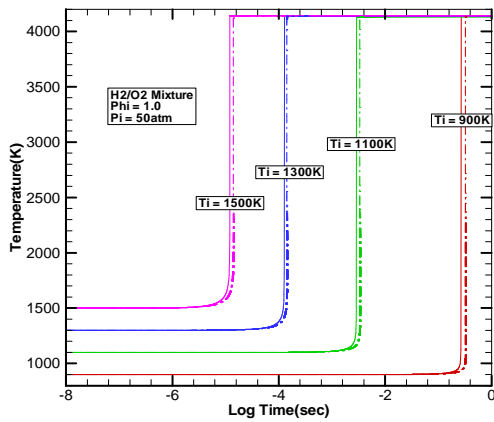

Fig.1: Temperature profiles for stoichiometric H₂/O₂ mixtures at p_i=50 atm and for varying initial temperatures.

For this range of initial conditions, the set results in predictions to within 5% accuracy against DKM calculations.
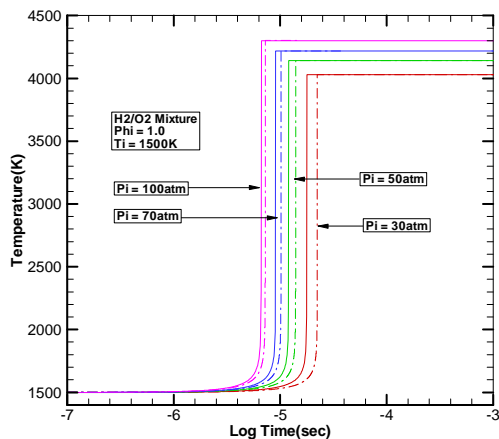

Fig.2: Temperature profiles for a stoichiometric mixture of H₂/O₂ at T_i=1500 K and different initial pressures.

CH₄/Air Model

The CH₄/air kinetic model includes 60 species and 352 chemical reactions. Ignition has been studied for an initial temperature ranging from 900 K to 1200 K and an initial pressure changing from 1 atm to 50 atm. The RCCE calculations were carried out using the 16 constraints in Table I. Comparison between DKM and RCCE has been performed and results are shown in figures 3 and 4 respectively. Although 16 equations (constraints) were used in the RCCE calculations versus 60 equations in the DKM calculations, RCCE predictions were within 5-10% of DKM's over the entire range of initial conditions. . The same level of agreements was found for the species profiles. Reference [13] can be consulted for more details.

C₂H₅OH/Air Model

The C₂H₅OH/air kinetic model includes 68 species and 383 chemical reactions. The RCCE calculations required only 16

constraints to model the ignition. These constraints are discussed in details in [13]. Ignition was studied over an initial temperature ranging from 1000 K to 1300 K and an initial pressure varying from 1 atm to 20 atm. Results are shown in figures 5 and 6 respectively. The RCCE predictions agree favourably well with those of DKM.
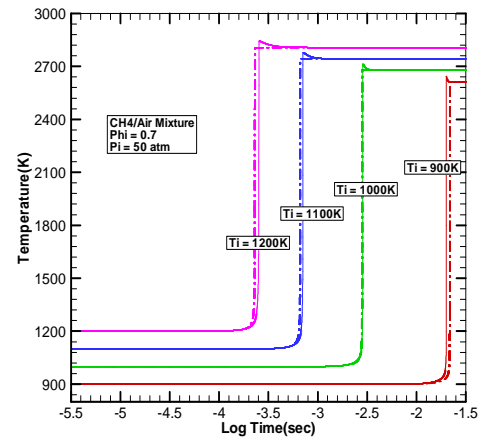

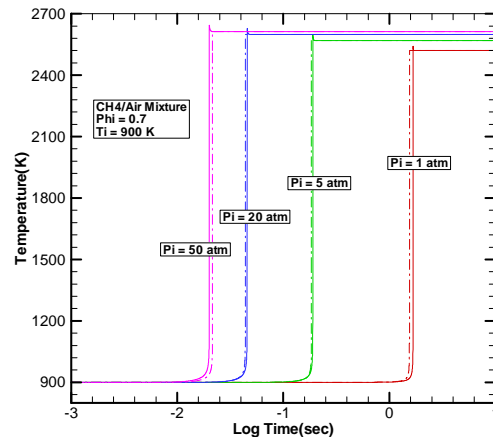Fig.3: Temperature profiles for lean CH₄/air mixtures at p_i = 50 atm and varying initial temperatures.

Fig.4: Temperature profiles for CH₄/air mixtures at T_i= 900 K and varying initial pressures.

CONCLUSIONS

RCCE calculations of H₂/O₂, CH4/air and C₂H₅OH/air have been conducted over a wide range of initial temperatures and initial pressures. Sets composed of 6, 16 and 16 constraints were used, respectively for each case and the results showed good agreements with detailed kinetic model predictions using 9, 60 and 68 species respectively. The RCCE models demonstrate consistent accuracies, within 5-10%, with respect to the corresponding detailed kinetic models.

The RCCE method offers several advantages among which are:
1. It is based on the Maximum Entropy or minimum free energy Principle of Thermodynamics rather than mathematical approximations.
2. The total number of constraints required to determine the non-equilibrium state of a system can be much smaller than the number of species in the system.
3. Every species for which the thermodynamic data is available can evolve dynamically based on the constrained-equilibrium requirement. This feature could be used to investigate whether a species, which is not explicitly included in the kinetic model, may be kinetically important or not.
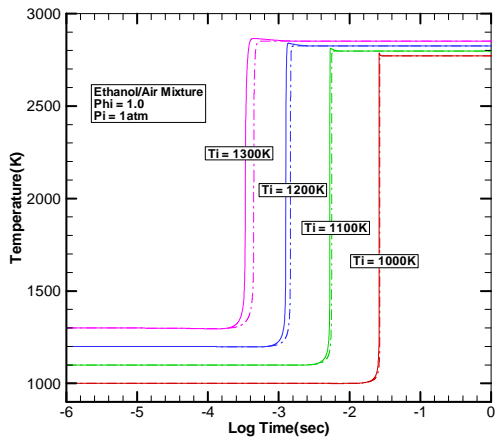
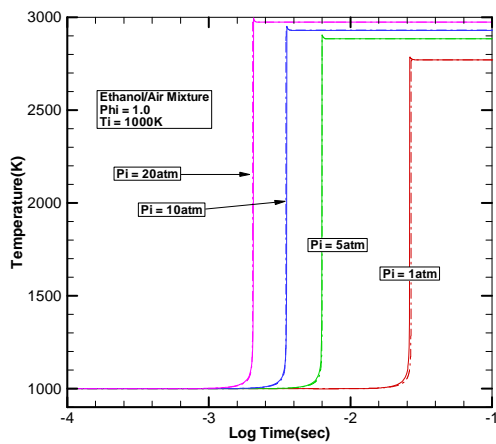Fig.5: Temperature profiles for C_2H_5OH/air mixture at p_i=1atm and varying initial temperatures.

Fig.6: Temperature profiles for C_2H_5OH/air mixtures at T_i=1000 K and varying initial pressures.

NOMENCLATURE

Symbol	Quantity	SI Unit
C_i	Constraint i	Unitless
a_{ij}	Value of constraint i for species j	Unitless
v_{jk}^+	Forward stoichiometric coefficient of species j for reaction k	Unitless
v_{jk}^-	Reverse stoichiometric coefficient of species j for reaction k	Unitless
r_k	Net rate of reaction k	$Mol.m^{-3}.s^{-1}$
N_r	Number of reaction	Unitless
N_c	Number of constraints	Unitless
N_{sp}	Number of species	Unitless
b_{ik}	The value of the ith constraint in k^{th} reaction	Unitless
γ_i	Constraint potential of constraint i	Unitless
μ_j^0	Non dimensional Gibbs free energy of species j	Unitless
R_u	Gas constant	$J.mol^{-1}.K^{-1}$
N_j	Number of Moles of species j	Mol
V	Volume	m^3
r_k^+	Forward rate of reaction k	$Mol.m^{-3}.s^{-1}$
r_k^-	Reverse rate of reaction k	$Mol.m^{-3}.s^{-1}$
$[N_j]$	Concentration of species j	$Mol.m^{-3}$
Q_j	Partition function of species j	Mole
T	Temperature	K

p_0	Atmospheric pressure	Pa
p	Pressure	Pa
E_j	Specific internal energy of species j	J
E	Total energy of the system	J
C_{vj}	Specific heat at constant volume for species j	$J.Kg^{-1}.K^{-1}$
t	time	s

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Table 1: List of constraints used

Constraints		Definition	H_2	CH_4	C_2H_5OH
1	EH	Total moles of Hydrogen element	✔	✔	✔
2	EO	Total moles of Oxygen element	✔	✔	✔
3	EC	Total moles of Carbon element	-	✔	✔
4	EN	Total moles of Nitrogen element	✔	✔	✔
5	M	Total number of moles	✔	✔	✔
6	FV	Moles of Free valance	✔	✔	✔
7	FO	Moles of Free Oxygen	✔	✔	✔
8	OHO	Moles of O+OH	-	✔	✔
9	DCO	Moles of HCO+CO	-	✔	✔
10	FU	Moles of fuel molecules (CH_4 or C_2H_5OH)	-	✔	✔
11	FR	Moles of fuel radicals (CH3 or $CH_3CHOH+CH_2CH_2OH+CH_3CH_2O$)	-	✔	✔
12	APO	Moles of alkyl peroxides ($CH_3OO+CH_3OOH+CH_2OOH$)	-	✔	-
13	ALCD	Moles of alcohols + aldehydes ($CH_3O+CH_3OH+CH_2OH+CH_2O$)	-	✔	✔
14	C_2H_6	Moles of C_2H_6	-	✔	✔
15	C-C	Moles of C-C bond	-	✔	✔
16	$C_2H_5+C_2H_4$	Moles of $C_2H_5+C_2H_4$	-	✔	✔